

The University of Chicago

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A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

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By
EDITH SAWYER HAMMOND

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The Ammines of Chromous Chloride

Chromous ammines were first prepared by Peters¹ by the action of gaseous ammonia on chromous chloride. His results were later partially verified by Ephraim,² who measured vapor tensions of the compounds at various temperatures. Although both investigators report the existence of a hexammine and a triammine, neither of them succeeded in causing the chromous chloride to add quite six moles of ammonia to one of the simple salt and they do not agree in their description of the color of the product. Furthermore, withdrawal of ammonia to form the triammine from the hexammine was not accompanied by an abrupt drop in the pressure as should have been the case had the measured tensions corresponded to equilibrium conditions.

Our preliminary experiments gave evidence of the existence of a pentammine and a diammine in addition to the compounds mentioned above, and showed that reinvestigation of the others was necessary to prove their existence definitely and to define their properties accurately. It very soon became obvious that the causes of the difficulty in the earlier work lay in the failure to use sufficiently purified samples of chromous chloride and to recognize the slowness with which equilibrium is attained.

Preparation of Chromous Chloride.—Chromous chloride was prepared by reducing chromic chloride with hydrogen at a furnace controlled temperature near 420°. The hydrogen was purified by passing it over hot platinized asbestos, then through a liquid air trap, followed by a phosphorus pentoxide tube, which had been evacuated and washed several times with hydrogen. The samples of chromic chloride used as starting material in the preliminary experiments were obtained by drying anhydrous chromic chloride in a stream of chlorine; for the final results, chromic chloride was resublimed in an atmosphere of pure chlorine before it was reduced. The chief difficulty is the prevention of secondary reduction of chromous chloride to chromium. The addition of hydrogen chloride to the hydrogen affords some protection against over reduction, but even under these conditions careful control of the temperature, and interruption of the reduction as soon as the color becomes pure white, are necessary. The chromous chloride thus obtained was transferred in an atmosphere of dry nitrogen to the reaction vessels in which it could be sealed, weighed and stored.

Preparation of Hexammine-Chromous Chloride.—The typical reaction vessel consisted of a glass tube about 14 × 200 millimeters, expanded at the lower end to a small flat bulb in which the chromous chloride could be spread over a fairly large area. The upper end was sealed after the chromous chloride had been introduced. Near the top was attached a side tube and stopcock through which the vessel was connected to a

(1) Peters, *Ber.*, **42**, 4833 (1909).

(2) Ephraim, *ibid.*, **50**, 535 (1917).

vacuum apparatus in which the ammonia pressure, as well as the volume of ammonia absorbed, could be measured.

After the tube containing chromous chloride was evacuated and weighed, pure dry ammonia at approximately 75 cm. pressure was admitted to the vessel. Absorption began at once with evolution of heat. To make certain that the reaction was complete, weighings were made only after the material showed no absorption for a period of about twenty-four hours. By deducting from the gain in weight of the vessel the weight of ammonia remaining in the gas phase, the amount of ammonia absorbed by the solid was obtained. In several experiments this weight was checked by measuring the volume of ammonia absorbed, but the gravimetric measurements proved more reliable. The data are reproduced in Table I.

TABLE I
COMPOSITION IN THE SYSTEM OF HEXAMMINE-CHROMOUS CHLORIDE

Sample number	Mole of chromous chloride	Approximate temperature, °C.	Final ammonia pressure, cm.	Ammonia absorbed, mole	Moles of ammonia per mole of CrCl_2
1	0.003448	27	46.35	0.02021	5.86
1	.003448	27	88.2	.02044	5.92
11	.001965	27	72.2	.01161	5.91
7	.001346	23	30.82	.00787	5.85
7	.001346	26	76.14	.00797	5.92
7	.001346	23	105.15	.00808	6.00
9	.001735	23	30.37	.01018	5.87
9	.001735	23	79.25	.01025	5.91
9	.001735	23	100.09	.01040	5.99
6	.001074	20	134.38	.00659	6.139
6	.001074	20	99.4	.00658	6.125
6	.001074	20	74.28	.006565	6.11
6	.001074	20	29.33	.00636	5.92
6	.001074	20	24.72	.00635	5.91
6	.001074	20	21.09	.00635	5.91
4	.001286	23	105.08	.00815	6.34
4	.001286	23	73.25	.00788	6.13
4	.001286	23	40.77	.00777	6.04
4	.001286	26	31.16	.00771	6.00
4	.001286	24	21.14	.00771	6.00

The table shows clearly the importance of using only the purest possible chromous chloride in experiments of this type. The data obtained with samples 1, 7, 9 and 11 which were made from unsublimed chromic chloride, while consistent among themselves, lead to the incorrect conclusion that absorption of six moles of ammonia does not occur until the pressure is near 100 cm. The more nearly pure the sample of chromous chloride, the lower the pressure required for the absorption of ammonia, as is seen from the experiment with sample No. 6 in which 5.91 moles of ammonia are taken up at pressures between 21 and 29 cm. The amount of ammonia absorbed by the most carefully purified sample (No. 4) is that required for the hexammine, and remains constant in a pressure range from about 20 to between 30 and 35 cm. At pressures below 18 cm., ammonia is again

lost and the color changes from deep blue to violet. These pressure values, however, represent merely convenient criteria for the preparation of the hexammine; the determination of the equilibrium pressures and definite evidence for the existence of the hexammine are described below.

Before turning to these measurements, a word should be said about the phenomena which accompany increase of the ammonia pressure beyond the limits mentioned above. At higher pressures the material becomes green, and when the pressure reaches 90 cm., gray. During these color changes small amounts of ammonia are absorbed very slowly; but even though the pressure is raised to 2 atmospheres and the temperature lowered to -15° , the maximum absorption corresponds to only 0.34 mole of ammonia in excess of that required for the hexammine. At present the most satisfactory explanation of these phenomena is that ammonia, first taken up as a solid solution, ammonolyzes the salt to the mixture of gray color. This interpretation is confirmed by the fact that the gray color cannot be discharged by decrease of the ammonia pressure, and that liquid ammonia extracts what appears to be ammonium chloride from the solid. The reaction, however, is so slow and incomplete that it could not be satisfactorily studied at the temperatures of our experiments.

It is evident from these results that Ephraim confused the gray color which resulted from the action of an excess of ammonia on the hexammine with the color of the hexammine itself. Furthermore, in experiments on dissociation pressures in this system the formation of the gray material must be avoided because it retards greatly the attainment of equilibrium and obscures the interpretation of analytical data. Unfortunately it is formed more rapidly at high temperatures, at which the dissociation pressures of the ammines would otherwise be more readily determined, and therefore the work must be done at temperatures at which the reactions are very slow.

The System Chromous Chloride-Ammonia.—Because of the difficulties just discussed, dissociation pressures of the various ammines could not be determined in the usual way by observing the pressures which are ultimately reached by mixtures of ammonia and chromous chloride ammines of various compositions. Instead, it was necessary in each case to prepare the mixture of hexammine and pentammine by allowing the former to remain in an evacuated vessel for a short period of time. Ammonia was then admitted and the pressure changes observed. If the pressure fell, its value obviously was above the dissociation pressure of the hexammine; consequently a portion of the gaseous ammonia was removed, and the observations were repeated. If the pressure continued to fall, more ammonia was removed from the gas phase. If the pressure rose, ammonia was readmitted but not in sufficient amount to bring the pressure back to its initial value. By repeated observations made after successive evacuations and readmissions of ammonia, the equilibrium value could be bracketed by approaching it from both sides. Finally an ammonia pressure could be found under which no changes occurred over a period of three or four days. This was taken as the equilibrium value. The procedure was very time-consuming, often requiring several weeks to establish a single point on the pressure composition diagram, but it led to reliable results. The

equilibrium pressures thus found at 35.5° are reproduced in Table II and Fig. 1.³ Compositions represent (moles NH_3)/(moles CrCl_2).

TABLE II

Compn.	5.85	5.3	5.19	4.95	4.81	4.54	3.6	3.2	2.95	2.21
Pressure, cm. Hg	23.25	23.25	23.25	3.5	3.5	3.5	3.5	3.5	0.85	0.85
	Hexammine			Pentammine					Triammine	

When the composition of the diammine is reached the pressure becomes immeasurably small, and further removal of ammonia cannot be effected even by raising the temperature to $140\text{--}150^\circ$ for twenty-four hours; at still higher temperatures ammonium chloride is given off. Inspection of the table and figure makes clear that chromous chloride forms amines

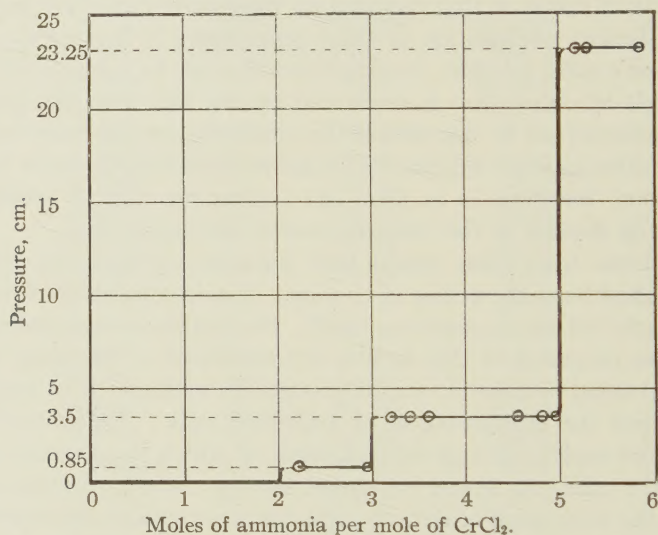


Fig. 1.—System chromous chloride—ammonia at 35.5° .

with 6, 5, 3 and 2 molecules of ammonia, respectively. The equilibrium pressures for the pentammine were also determined at 41 and 50° and found to be 5.7 and 10.3 cm., respectively; for the triammine the value is 5.38 cm. at 62° . These values are obtained from measurements at a single composition in each case. Since only two measurements were made for the triammine at 35.5° , because of the slowness with which equilibrium is reached at this temperature, measurements at the compositions 2.95, 2.54, 2.3 and 2.21 were made at 42° , and gave the constant value 1.1 cm. This confirms the conclusion drawn on the basis of the small number of determinations at the lower temperature.

Preparation of the Lower Amines.—The dissociation pressures show

(3) In interpreting the curve it should be borne in mind that the abrupt changes shown in the pressure are changes in the equilibrium values. At no composition is there a rapid transition from one constant pressure to another.

that the data of both Peters and Ephraim are erroneous in several respects, for they recognized only a hexammine and a triammine. In many instances their data do not correspond to equilibrium conditions.⁴ Ephraim's failure to obtain a constant vapor tension as ammonia is removed from the hexammine has been shown to be due to an extremely slow attainment of equilibrium. He also assigns to the triammine the vapor tension which, according to our results, is more nearly that of the pentammine. Our observations also indicate confusion in the earlier descriptions of the properties of the ammines, particularly with regard to their colors. It was, therefore, desirable to prepare each of them in as pure condition as possible.

If a vessel containing a sample of the hexammine is continuously evacuated at room temperature, the pressure falls steadily to about four millimeters, during which time there is a gradual change in color from blue to deep violet. The hexammine is thus completely decomposed; small amounts of ammines other than the pentammine are removed by allowing the material to stand for some time in contact with ammonia at a pressure just below the dissociation pressure of the hexammine.

Removal of ammonia from the pentammine is much hastened by raising the temperature to 60 or 70°. If the sample is not heated too long, the gray material described above is not formed in appreciable quantity, probably because of the low pressure at which removal is effected. At a composition of approximately three moles of ammonia to one of chromous chloride, the color has changed again, this time to a light blue, and the equilibrium pressure has changed to that of the triammine. In similar fashion the sage green diammine can be prepared. The data concerning these ammines are summarized in Table III.

TABLE III

Ammine	Analysis, ^a moles NH ₃ per mole CrCl ₂	Dissociation pressure, cm. ^b	Color
CrCl ₂ .6NH ₃	6.01	23.25	Dark blue
CrCl ₂ .5NH ₃	4.95	3.5	Violet
CrCl ₂ .3NH ₃	3.03	0.85	Light blue
CrCl ₂ .2NH ₃	2.00	Practically zero	Sage-green

^a Calculated from the average of data obtained from the purest sample.

^b Values for the dissociation pressures at other temperatures are given on p. 3974.

The Reactions of Chromous Chloride Ammines with Chlorine.—It seemed possible that reaction of chlorine with the diammine, which because of its low ammonia tension is particularly suited to such a study, might lead to the formation of a diammine of chromic chloride. This

(4) Ephraim gives the vapor tension of the hexammine as

Temperature, °C.	0	13	16	27	33.5	43.5
Pressure, mm.	104	194	228	387	517	744

For the violet intermediate product which he calls the triammine, he gives the following tensions

Temperature, °C.	44	59.5	72	86	92	95
Pressure, mm.	45	97	198	433	618	730

substance would have peculiar interest because the normal coördination number of trivalent chromium is six. For carrying out the reaction, the reaction tube was connected into a closed system provided with a manometer in which the mercury was protected from the chlorine by a small layer of concentrated sulfuric acid. The system was evacuated and pure dry chlorine admitted. There was no apparent reaction in the cold, but at 250° the absorption of chlorine became noticeable and resulted in the formation of a reddish-violet hygroscopic substance which was unstable in air. At approximately 275° the color changed to a deep purple and ammonium chloride was evolved. At still higher temperatures complete reaction to form chromous chloride, ammonium chloride and nitrogen occurred. All the intermediate stages seemed to be mixtures of variable composition.

The fact that chlorine should oxidize the ammonia in the complex molecule without affecting the powerfully reducing chromous ion was unexpected. A similar reaction occurs with the triamine; this may be due to the fact that by oxidation of ammonia the diamine is first formed and then reacts further with chlorine. The essential reaction of chlorine with the amines is oxidation of the ammonia; the color changes were shown by direct test to be due to interaction of hydrogen chloride formed by this oxidation, on the residual amines. The product of the reaction of hydrogen chloride on the amines is a mixture which could not be separated into its components.⁵

The writer wishes to acknowledge her indebtedness to Dr. H. I. Schlesinger at whose suggestion and under whose direction this work was carried on. She is also indebted to Dr. Warren Johnson and Dr. Anton Burg for helpful assistance during the course of the work.

Summary

A blue hexamine, a violet pentamine, a light blue triamine, and a sage-green diamine of chromous chloride were prepared.

Methods were developed for determining the dissociation pressures of these substances in spite of the fact that equilibrium is attained very slowly. Dissociation pressures of $\text{CrCl}_2 \cdot 6\text{NH}_3$, for $\text{CrCl}_2 \cdot 5\text{NH}_3$, and for $\text{CrCl}_2 \cdot 3\text{NH}_3$ were determined at 35.5° ; in addition ammonia tensions for the pentamine were measured at 41 and 50° , and for the triamine at 42 and 62° .

Chlorine oxidizes the ammonia of these complex chromous compounds but does not affect the chromous nucleus.

(5) Analysis of the first sample of this material showed the following ratio: chromium 1, ammonia 1.488, chlorine 3.55. This would indicate the formation of a compound of the type $2\text{CrCl}_2 \cdot 3\text{NH}_4\text{Cl}$. Later samples failed to duplicate first results.

